



(11) **EP 2 047 335 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention
of the grant of the patent:
11.05.2011 Bulletin 2011/19

(51) Int Cl.:
G03G 9/08 ^(2006.01) **G03G 9/12** ^(2006.01)
G03G 9/09 ^(2006.01)

(21) Application number: **06788368.6**

(86) International application number:
PCT/US2006/028758

(22) Date of filing: **25.07.2006**

(87) International publication number:
WO 2008/013522 (31.01.2008 Gazette 2008/05)

(54) **METHODS OF PRODUCING INK TONERS**

VERFAHREN ZUM HERSTELLEN VON TINTENTONERN

PROCÉDÉS DE FABRICATION DE TONERS D'ENCRE

(84) Designated Contracting States:
DE GB

(43) Date of publication of application:
15.04.2009 Bulletin 2009/16

(73) Proprietor: **HEWLETT-PACKARD DEVELOPMENT
COMPANY, L.P.**
Houston, TX 77070 (US)

(72) Inventors:
• **GAL, Victor**
76101 Rehovot (IL)
• **SCHEFFER, Dan**
76101 Rehovot (IL)

- **GOLODETZ, Galia**
76101 Rehovot XX (IL)
- **KUPERWASSER, Jose**
76101 Rehovot (IL)
- **KATZ, Natalia**
76101 Rehovot (IL)

(74) Representative: **Johnston, Magnus George et al**
Haseltine Lake LLP
Redcliff Quay
120 Redcliff Street
Bristol BS1 6HU (GB)

(56) References cited:
EP-A- 1 204 005 EP-A2- 0 424 093
US-A1- 6 117 606

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 2 047 335 B1

Description

BACKGROUND

5 **[0001]** Various techniques for electrostatic image transfer are known. One method includes the use of an intermediate transfer member. A liquid image, which includes a liquid carrier having ink particles dispersed therein, is transferred from a photoconductive surface of a photoconductive member or drum to a surface (e.g., a release layer or blanket) of the intermediate transfer member. The liquid image is attracted from the photoconductive surface to the surface of the intermediate transfer member. The liquid carrier is removed from the surface of the intermediate transfer member and the ink particles are compacted on the surface in the image configuration. Thereafter, the ink particles are transferred from the surface of the intermediate transfer member to a substrate in the image configuration by electrostatic attraction.

10 **[0002]** Modern liquid toner electrostatic imaging began with the invention of a new class of toners referred to as Electroink™. This type of toner is characterized by its toner particles being dispersed in a carrier liquid, where the toner particles include a core of a polymer with fibrous extensions extending from the core. When the toner particles are dispersed in the carrier liquid in a low concentration, the particles remain separate. When the toner develops an electrostatic image, the concentration of toner particles increases and the fibrous extensions interlock. A large number of patents and patent applications are directed toward this type of toner (e.g., U.S. Pat. Nos. 4,794,651; 4,842,974; 5,047,306; 5,407,307; 5,192,638; 5,208,130; 5,225,306; 5,264,312; 5,266,435; 5,286,593; 5,300,390; 5,346,796; 5,407,771; 5,554,476; 5,655,194; 5,792,584 and 5,5923,929 and PCT Patent publication WO/92/17823).

20 **[0003]** It has been discovered that this type of toner allows for high quality offset printing at high speed. This type of printing is described the following patents 4,678,317; 4,860,924; 4,980,259; 4,985,732; 5,028,964; 5,034,778; 5,047,808; 5,078,504; 5,117,263; 5,148,222; 5,157,238; 5,166,734; 5,208,130; 5,231,454; 5,255,058; 5,266,435; 5,268,687; 5,270,776; 5,276,492; 5,278,615; 5,280,326; 5,286,948; 5,289,238; 5,315,321; 5,335,054; 5,337,131; 5,376,491; 5,380,611; 5,426,491; 5,436,706; 5,497,222; 5,508,790; 5,527,652; 5,552,875; 5,555,185; 5,557,376; 5,558,970; and 5,570,193.

25 **[0004]** US 6,117,606 discloses C.I. Pigment Yellow 155 used as a colorant in electrophotographic toners and developers, powder coating materials, inkjet inks, color filters and electret materials.

[0005] Color shifting pigments and colorants (e.g., special-effect pigments) have been used in numerous applications, ranging from automobile paints to anti-counterfeiting inks for security documents and currency. Such pigments and colorants exhibit the property of changing color upon variation of the angle of incident light, or as the viewing angle of the observer is shifted. The primary method used to achieve such color shifting colorants is by dispersing small flakes, which are typically comprised of multiple layers of thin films having particular optical characteristics, throughout a medium such as paint or ink that may then be subsequently applied to the surface of an object.

30 **[0006]** The color shifting properties of the colorant can be controlled through proper design of the optical coatings or films used to form the flakes. Desired effects can be achieved through the variation of parameters such as thickness of the layers forming the flakes and the index of refraction of each layer. The changes in perceived color which occur for different viewing angles or angles of incident light are a result of a combination of selective absorption of the materials including the layers and wavelength dependent interference effects. The absorption characteristics of a material as well as interference phenomena are responsible for the basic color that is observed. The interference effects, which arise from the superposition of the light waves that have undergone multiple reflections and transmissions within the multi-layered thin film structure, are responsible for the shifts in perceived color with different angles. Thus, use of the special-effect pigments requires that the layers of the special-effect pigments be intact in the ink formulation.

SUMMARY

45 **[0007]** Briefly described, embodiments of this disclosure includes methods of making ink toners for use in electrostatic imaging and ink compositions including the ink toners. The method of forming an ink toner comprises: mixing a carrier liquid and a resin to form a slurry; grinding the slurry for 1 to 5 hours at 50° C to 60° C at 500 to 800 revolutions per minute (RPM); reducing the grinding to 25 to 150 RPM; adding a pigment to the slurry and grind until the pigment is absorbed in the slurry to form a slurry/pigment mixture, wherein the pigment is selected from optically variable pigments, thermochromic pigments, photochromic pigments, photo luminescent pigments, and combinations thereof; and grinding the slurry/pigment mixture at 500 to 800 RPM for 15 to 45 minutes at 25° C to 35° C to form the ink toner.

BRIEF DESCRIPTION OF THE DRAWINGS

55 **[0008]** Many aspects of this disclosure can be better understood with reference to the following drawings. The components in the drawings are not necessarily to scale. Moreover, in the drawings, like reference numerals designate corresponding parts throughout the several views.

FIG. 1 illustrates a flow chart of an embodiment of a method for making optically variable ink toners.

FIG. 2 illustrates a flow chart of an embodiment of a method for making optically variable ink toners.

DETAILED DESCRIPTION

[0009] Embodiments of the present disclosure will employ, unless otherwise indicated, techniques of synthetic organic chemistry, ink chemistry, media chemistry, printing chemistry, and the like, that are within the skill of the art. Such techniques are explained fully in the literature.

[0010] The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how to perform the methods and use the compositions disclosed and claimed herein. Efforts have been made to ensure accuracy with respect to numbers (*e.g.*, amounts, temperature, etc.) but some errors and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight, temperature is in °C, and pressure is at or near atmospheric. Standard temperature and pressure are defined as 20 °C and 1 atmosphere.

[0011] It must be noted that, as used in the specification and the appended claims, the singular forms "a," "an," and "the" include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a support" includes a plurality of supports. In this specification and in the claims that follow, reference will be made to a number of terms that shall be defined to have the following meanings unless a contrary intention is apparent.

Discussion

[0012] Embodiments of the present disclosure include methods of making ink toners and ink compositions for use in electrostatic imaging, where the ink toner includes a pigment that may not be able to be processed under normal conditions. The pigment can include, but is not limited to, optically variable pigments, thermochromic pigments, photochromic pigments, photo luminescent pigments, phosphorescent pigments, brittle pigments, crystalline pigments, or combinations thereof. Current methods of making optically variable ink toners for use in electrostatic imaging are not operable. Current methods destroy the pigments present in the ink toner. For example, one or more of the layers that make up optically variable pigments are destroyed during the grinding procedures used in the current methods. For reasons of clarity, reference will be made to optically variable pigments to describe embodiments of the present disclosure, but one or more of the pigments mentioned above can be substituted for (or combined with) the optically variable pigment in the embodiments described herein.

[0013] Current methods include mixing the optically variable pigment with a carrier liquid and a resin. The mixture is ground at about 700 revolutions per minute (RPM). The grinding causes one or more of the layers of the optically variable pigment to crack, flake off, or otherwise be damaged. The layers of the optically variable pigment provide the goniochromatic effect, metal effect, and/or interference effect for optically variable pigments.

[0014] Embodiments of the present disclosure include reducing the grinding speed (RPM) when the optically variable pigment is added to a pre-toner mixture. The reduced grinding speed allows the optically variable pigment to be absorbed into the pre-toner mixture. Then, once the optically variable pigment is absorbed into the pre-toner mixture, the grinding speed is increased and, ultimately a toner is produced that includes the optically variable pigment.

[0015] FIG. 1 illustrates a flow chart of an embodiment of a method 10 for making optically variable ink toners. Block 12 indicates that a slurry (also referred to as "pre-toner mixture") including a carrier liquid and a resin is ground at a normal speed, which is about 700 RPM. Other components such as, but not limited to, a charge adjuvant, organic/inorganic pigment, surface modifiers and additives, can be added to the slurry at this stage.

[0016] Block 14 indicates that the grinding speed is significantly reduced (*e.g.*, 25 to 150 RPM) and an optically variable pigment is added to the slurry and mixed until the optically variable pigment is completely absorbed into the slurry. Other components such as, but not limited to, a charge adjuvant, organic/inorganic pigment, surface modifiers, and additives, can be added to the slurry at this stage. Block 16 indicates that the grinding speed is increased to a normal level and the slurry/pigment is ground for a period of time and temperature. The final product, an optically variable ink toner, is removed after the slurry/pigment is ground.

[0017] FIG. 2 illustrates a flow chart of an embodiment of a method 20 for making optically variable ink toners. Block 22 indicates that a carrier liquid and a resin are mixed in a mixer (*e.g.*, double planetary mixer) for 1 to 3 hours (or about 1.5 hours) at a temperature of 120° C to 160° C. Other components such as, but not limited to, a charge adjuvant, organic/inorganic pigment, surface modifiers, and additives, can be added to the slurry at this stage.

[0018] Block 24 indicates that the slurry is mixed for an additional 1 to 5 hours (or about 1.5 hours) to cool the slurry to 25° C to 35° C. Block 26 indicates that the slurry is added to a grinder (*e.g.*, an attritor, a disk mill, a sand mill, an impeller attrition mill, a vibro-energy mill). Other components such as, but not limited to, a charge adjuvant, organic/inorganic pigment, surface modifiers, and additives, can be added to the slurry at this stage.

[0019] Block 28 indicates that the slurry is ground for 3 to 8 hours (*e.g.*, 4 to 6 hours or about 5 hours) at 50° C to 60° C at 500 to 800 RPM (*e.g.*, 600 to 800 RPM or about 700 RPM). Block 32 indicates that the grinding speed is reduced

to 25 to 150 RPM (e.g., 25 to 100 RPM, 40 to 60 RPM, or about 50 RPM) and then an optically variable pigment is added to the mixer. Other components such as, but not limited to, a charge adjuvant, organic/inorganic pigment, surface modifiers, and additives, can be added to the slurry at this stage.

[0020] Block 34 indicates that the slurry and pigment mixture is ground until the optically variable pigment is completely absorbed (e.g., the optically variable pigment is not observed) into the slurry, which is 5 to 10 minutes. Block 36 indicates that the grinding is increased to 500 to 800 RPM (e.g., 600 to 800 RPM or about 700 RPM) for 10 to 40 minutes (about 30 minutes) at 25° C to 35° C. The optically variable ink toner is removed after the slurry/pigment is ground.

[0021] As mentioned above, the liquid carrier and the resin mixed to form a slurry. The carrier liquid can include, but is not limited to, an insulating, nonpolar liquid that is used as the medium for toner particles. The carrier liquid can include compounds that have a resistivity in excess of 10⁹ ohm-cm and a dielectric constant below 3.0. The carrier liquid can include, but is not limited to, hydrocarbons. The hydrocarbon can include, but is not limited to, an aliphatic hydrocarbon, an isomerized aliphatic hydrocarbon, branched chain aliphatic hydrocarbons, aromatic hydrocarbons, and combinations thereof.

[0022] Illustrative carrier liquids include, but are not limited to, aliphatic hydrocarbon, isoparaffinic compounds, paraffinic compounds, dearomatized hydrocarbon compounds. In particular, the carrier liquids can include, but are not limited to, Isopar-G™, Isopar-H™, Isopar-L™, Isopar-M™, Isopar-K™, Isopar-V™, Norpar 12™, Norpar 13™, Norpar 15™, Exxol D40™, Exxol D80™, Exxol D100™, Exxol D130™, and Exxol D140™ (each sold by EXXON CORPORATION); Teclen N-16™, Teclen N-20™, Teclen N-22™, Nisseki Naphthesol L™, Nisseki Naphthesol M™, Nisseki Naphthesol H™, #0 Solvent L™, #0 Solvent M™, #0 Solvent H™, Nisseki Isosol 300™, Nisseki Isosol 400™, AF-4™, AF-5™, AF-6™ and AF-7™ (each sold by NIPPON OIL CORPORATION); IP Solvent 1620™ and IP Solvent 2028™ (each sold by IDEMITSU PETROCHEMICAL CO., LTD.); Amsco OMS™ and Amsco 460™ (each sold by AMERICAN MINERAL SPIRITS CORP.); and electron, positron, new II, purogen HF (100% synthetic terpenes) (sold by ECOLINK).

[0023] The carrier liquid is 20 to 95% by total weight of the slurry, 40 to 90% by total weight of the slurry, and 60 to 80% by total weight of the slurry.

[0024] The resin can include, but is not limited to, thermoplastic toner resins. In particular, the resin can include, but is not limited to, ethylene acid copolymers; ethylene acrylic acid copolymers; methacrylic acid copolymers; ethylene vinyl acetate copolymers; copolymers of ethylene (80 to 99.9%), acrylic, or methacrylic acid (20 to 0.1%)/alkyl (C1 to C5) ester of methacrylic or acrylic acid (0.1 to 20%); polyethylene; polystyrene; isotactic polypropylene (crystalline); ethylene ethyl acrylate; polyesters; polyvinyl toluene; polyamides; styrene/butadiene copolymers; epoxy resins; acrylic resins (e.g., copolymer of acrylic or methacrylic acid and at least one alkyl ester of acrylic or methacrylic acid wherein alkyl is from 1 to about 20 carbon atoms, like methyl methacrylate (50 to 90%)/methacrylic acid (0 to 20 percent)/ethylhexylacrylate (10 to 50%)); ethylene-acrylate terpolymers: ethylene-acrylic esters-maleic anhydride (MAH) or glycidyl methacrylate (GMA) terpolymers; low molecular weight ethylene-acrylic acid ionomers and combinations thereof. In an embodiment, the toner can include the Nucrel family of toners (e.g., Nucrel 403™, Nucrel 407™, Nucrel 609HS™, Nucrel 908HS™, Nucrel 1202HC™, Nucrel 30707™, Nucrel 1214™, Nucrel 903™, Nucrel 3990™, Nucrel 910™, Nucrel 925™, Nucrel 699™, Nucrel 599™, Nucrel 960™, Nucrel RX 76™, Nucrel 2806™, Bynell 2002, Bynell 2014, and Bynell 2020 (sold by E. I. du PONT)), the Aclyn family of toners (e.g. Aaclyn 201, Aclyn 246, Aclyn 285, and Aclyn 295), and the Lotader family of toners (e.g. Lotader 2210, Lotader, 3430, and Lotader 8200 (sold by Arkema)).

[0025] The resin is 5% to 80% by total weight of the slurry, 10 to 60 by total weight of the slurry, and 15 to 40% by total weight of the slurry.

[0026] As mentioned above, the charge adjuvant, and optically variable pigment are mixed with the slurry in an attritor. The charge adjuvant can include, but is not limited to, barium petronate, calcium petronate, Co salts of naphthenic acid, Ca salts of naphthenic acid, Cu salts of naphthenic acid, Mn salts of naphthenic acid, Ni salts of naphthenic acid, Zn salts of naphthenic acid, Fe salts of naphthenic acid, Ba salts of stearic acid, Co salts of stearic acid, Pb salts of stearic acid, Zn salts of stearic acid, Al salts of stearic acid, Zn salts of stearic acid, Cu salts of stearic acid, Pb salts of stearic acid, Fe salts of stearic acid, divalent metal carboxylates and trivalent metal carboxylates (e.g., Al tristearate, Al octanoate, Li heptanoate, Fe stearate, Fe distearate, Ba stearate, Cr stearate, Mg octanoate, Ca stearate, Fe naphthenate, Zn naphthenate, Mn heptanoate, Zn heptanoate, Ba octanoate, Al octanoate, Co octanoate, Mn octanoate, and Zn octanoate), Co lineolates, Mn lineolates, Pb lineolates, Zn lineolates, Ca oleates, Co oleates, Zn palmirate, Ca resinate, Co resinate, Mn resinate, Pb resinate, Zn resinate, AB diblock copolymers of 2-ethylhexyl methacrylate-co-methacrylic acid calcium and ammonium salts, copolymers of an alkyl acrylamidoglycolate alkyl ether (e.g., methyl acrylamidoglycolate methyl ether-co-vinyl acetate), hydroxy bis(3,5-di-tert-butyl salicylic) aluminate monohydrate, and a mixture of hydroxy bis(3,5-di-tert-butyl salicylic) aluminate monohydrate. In an embodiment, the charge adjuvant is aluminum tristearate.

[0027] The charge adjuvant is 0.1 to 5% by total weight of the solid, 0.5 to 4% by total weight of the solid, and 1 to 3% by total weight of the solid.

[0028] As mentioned above, the pigment can include pigments that can be damaged or made inoperable during normal toner making processes. The pigment can include, but is not limited to, optically variable pigments, thermochromic

pigments, photochromic pigments, phosphorescent pigments, electroluminescent pigments, photoluminescent pigments, and combinations thereof.

[0029] The optically variable pigment or special-effect pigment can include, but is not limited to, metal effect pigments, interference pigments, luster pigments, goniochromatic pigments, pearlescent pigments, and pigments that exhibits a change in color based on the angle of observation. By metal effect pigment is meant a pigment giving a metallic coloration and appearance. By interference pigment is meant a pigment giving an interference effect. The special-effect pigment is preferably a customary commercial metal-effect pigment (e.g., platelet-shaped iron oxide, aluminum flakes, Stapa-Alupaste™, and Standart™ each can be purchased from Eckart), special-effect pigments (e.g., Paliochrom™ which can be purchased from BASF), and pearl luster pigments (e.g., mica flake pigments coated with metal oxides, Iriodin™ each of which can be purchased from Merck KGaA, Darmstadt). The mica flake pigments coated with metal oxides are known, for example, from the German Patents and Patent Applications 14 67 468; 19 59 998; 20 09 566; 22 14 545; 22 15 191; 22 44 298; 23 13 331; 25 22 572; 31 37 808; 31 37 809; 31 51 343; 31 51 354; 31 51 355; 32 11 602; and 32 53 017.

[0030] The thermochromic pigments and/or photochromic pigments can include, but are not limited to, Thermochromic BT-31, Thermochromic VT-31, PhotoChromic BL-60S, and PhotoChromic VL-70S (trademarks owned and products sold by KELLY CHEMICAL CORP.); Covapearl Sparkling Silver 937 AS, Covapearl Silver 939 AS, Covapearl Sparkling Gold 238 AS, Covapearl Fire Red 333 AS, Covapearl Antique Silver 239 AS, Covapearl Bright 933 AS, Covapearl Satin 931 AS, Covapearl Antique 236 AS, Covapearl Pink 433 AS, Covapearl Red 339 AS, and Covapearl Blue 635 AS (trademarks owned and products sold by Adina Cosmetics); Aztec Gold --305, Rutile sterling 103 and 108, Silk Pearl 173, Bronze Satin 310, Rutile Luster satin 121 and 130, Fine Gold Satin 201, Wine Red Satin 524, Wine Red Satin 224, Bronze Satin 530, Fine Gold Satin 201, Platinum Pearl 205, and Special Flash Pearl 183 (trademarks owned and products sold by Zhejiang Aoke pearlescent Pigment Co., Ltd); KTZ Roussillon -TTB2, KTZ Aruban Coral - 12, KTZ Aruban Cora, KTZ Shimmer White, KTZ Stellar White 11 S2, and KTZ Jaipur Sunset (trademarks owned and products sold by Kobo Products Inc.); XYMARA PEARL 103 XYMARA™ Marker Green SF1A, XYMARA™ Marker Ice Blue SF2A, XYMARA™ Marker Turquoise LF1A (sold by CIBA); DECO IRIS-GLITTER 2701-322-11 hex RAINBOW (sold by SiLi - SIGMUND LINDER GmbH); VA-516 Yellow and VA-515 Yellow Orange (sold by Vicome Corp.); KW 421 Magic yellow, KW 163 Shimmer Pearl, KW 289 Glitter Blue, KW 534 Shimmer Wine Red, KW 400B Luster Pure Blue, and KW 483 Silky Purple; (trademarks owned and products sold by WENZHOU KUNWEI PEARL PIGMENTS CO.); StarLight HM72, StarLight SM26, and StarLight FL500 (trademarks owned and products sold by SHEPHERD); 933 AS, 339AS, 238AS, 939AS, 635AS, 931AS, 239AS, 333AS, 937AS, 433AS, and 236AS (trademarks owned and products sold by SENSIENT COSMETIC TECHNOLOGIES); Mearlin Hi-Lite Sparkle Gold, Mearlin Hi-Lite Sparkle Violet, Mearlin Hi-Lite Sparkle Green, Mearlin Firemist Pearl, Mearlin Firemist Violet, and Mearlin Firemist Green (trademarks owned and products sold by ENGELHARD); Deco Iris-Glitter 2701-322-11hex, Rainbow Polyester-Glitter 2501-81E-1hex, Yellow Deco-Polyester Glitter 2701-67-11 hex, Multi Deco Hologramm 2701-59A-11hex, Copper Deco-Iris Glitter 2701-300FM-11hex, Way Too Pink Alu-Glitter 2101-54-1sq, Royal Blue Alu-Glitter 2110-50-1sq, Bright Silver Alu-Glitter 2101-43-1sq, and Rich Red Gold (trademarks owned and products sold by SIGMUND LINDER GmbH); and those shown in Table 1 below (trademarks owned and products sold by Clariant).

Table 1

<u>Gold Luster</u>			
Satin Gold 302	Sunny Gold 351	Solar Gold 305	Royal Gold 303
Satin Green 302	Sunny Green 351	Solar Green 305	Royal Green 303
Satin Orange 302	Sunny Orange 351	Solar Orange 305	Royal Orange 303
Satin Black 302	Sunny Black 351	Solar Black 305	Royal Black 303
<u>White Luster</u>			
Satin Gold 302	Sunny Gold 351	Solar Gold 305	Royal Gold 303
Satin Green 302	Sunny Green 351	Solar Green 305	Royal Green 303
Satin Orange 302	Sunny Orange 351	Solar Orange 305	Royal Orange 303
Satin Black 302	Sunny Black 351	Solar Black 305	Royal Black 303
<u>Metal Luster</u>			
Yellow Satin 520	Rose Gold Satin 520	CoR-PP18er Satin 522	Red Satin 524

EP 2 047 335 B1

(continued)

5	<u>Metal Luster</u>			
	Gold Satin 520	Bronze Satin 520	Brown Satin 522	Volcanic Satin 524
	Silver A 123	Silver B 123	Silver C 123	Silver D 123
10	Sterling Silver A 103	Sterling Silver B 103	Sterling Silver C 103	Sterling Silver D 103
	<u>Classic</u>			
	White Classic 201	White Classic 231	White Classic 211	White Classic 221
15	Orange Classic 201	Yellow Classic 231	Yellow Classic 211	Red Classic 221
	Green Classic 201	Blue Classic 231	Blue Classic 211	Green Classic 221
	Gold Classic 201	Green Classic 231	Red Classic 211	Blue Classic 221
20	<u>FLASH</u>			
	White Flash 249	White Flash 299	White Flash 259	White Flash 289
	Yellow Flash 249	Green Flash 299	Red Flash 259	Blue Flash 289
25	Green Flash 249	Blue Flash 299	Yellow Flash 259	Red Flash 289
	Black Flash 249	Black Flash 299	Black Flash 259	Black Flash 289
	<u>MULTI INTERFERENCE</u>			
30	White Multi T20	Blue Multi T20	Blue Flash S 105	Blue Classic S 105
	Yellow Multi T20	Blue/Green Multi T20	Green Flash S 105	Green Classic S 105
	Red Multi T20	Green Multi T20	Yellow Flash S 105	Red Classic S 105
35	Pink Multi T20	Black Multi T20	Red Flash S 105	Gold Classic S 105
	<u>GLITTER</u>			
	Shimmer Pearl 163	Gold Glitter 355	Red Shimmer 163	Green Flash 153
40	Gold 43E	Rose Gold 7E	Orange Gold 8E	Cherrywood 41 E
	Purple 13E	Emerald 20E	Peacock 16E	Black Fox 32E
	Bright Silver 140	Bright Silver 160	Bright Silver 100	Sparkle Pearl 183
45	<u>SPARKLE</u>			
	White Star 105	Yellow Star 105	Red Star 500	Blue Star 500
	Gold Star 105	Magenta Star 105	Orange Star 500	Purple Star 500
50	CoR-PP18er Star 105	Green Star 105	Yellow Star 500	Magenta Star 500
	Volcanic Star 105	Black Star 105	Green Star 500	Black Star 500

[0031] The photo luminescent can include, but are not limited to, Green VGS3-FAP (trademarks owned and products sold by VISIOGLOW); UPO-9D, UPO-9C, UPO-9E, UPB7E, RC-8C, and ROR-8C (trademarks owned and products sold by HANGZHOU UNION PIGMENT Co.), Phosphor H10 (trademarks owned and products sold by H13Cleveland Pigment & Color), and Luminova GLL-300FFS (trademarks owned and products sold by NEMOTO PORTUGAL). The electroluminescent pigments can include, but are not limited to, Glaciorglo GG25X1009 Blue/Green (trademarks owned and products sold by OSRAM SYLVANIA).

[0032] The optically variable pigment is 5% to 80% by total weight of the solid, 10 to 70% by total weight of the solid, and 30 to 60% by total weight of the solid.

[0033] In an embodiment the optically variable ink toner, the final product is 0.85 to 56.4 weight % of resin, 0.25 to 48 weight % of the optically variable pigment, 0.05 to 1.8 weight percent of the charge adjuvant, and 40 to 95 weight % of liquid carrier (e.g., the amount of liquid carrier is adjusted to modify the viscosity of the toner).

[0034] In an embodiment the optically variable ink toner, the final product is 47 to 69 weight % of resin, 30 to 60 weight % of the optically variable pigment, 1 to 3 weight percent of the charge adjuvant, and an amount of liquid carrier to modify the viscosity of the toner to the appropriate viscosity.

[0035] It should also be noted that embodiments of this disclosure provide for ink toners that may be used for security

applications such as optically variable inks, specifically activated under ultra violet (UV) radiation inks (e.g., visible if exposed to specific UV wave length), phosphorescent inks, "double-security effect" inks (e.g., phosphorescent in the dark (glow in the dark) and visible under UV radiation, electroluminescent inks and thermo/photo inks).

[0036] While embodiments of the present disclosure are described in connection with Example 1 and the corresponding text and figures, there is no intent to limit the disclosure to the embodiments in these descriptions.

Example 1

[0037] In an illustrative embodiment, a toner including an optically variable pigment may be prepared by preparing a mixture of a carrier liquid such as Isopar-L™ (60%-85%, by total weight), a resin such as Nucrel™ 699 (15%-40%, by total weight). The ingredients are mixed in a double planetary mixer, for example a Ross mixer, for about 1.5 hours at a temperature between 120° C to 160° C to produce a slurry of the carrier and polymer particles plasticized by solvation of the liquid carrier. The mixing is then continued for another 1.5 hours while the mixture cools down to room temperature. The slurry (50%-90%, by total weight of solids) is then added to a 750 ml attritor (e.g., a Union Process™ MODEL 01-HD ATTRITOR) together with a charge adjuvant like aluminum tristearate (1%-5%, by total weight of solids). Isopar-L™ can be added to adjust the viscosity of the slurry. The slurry is ground for 5 hours at 50°C-60°C at about 700 RPM. After this the RPM is lowered to about 50 RPM and a pigment such as Iriodin 7235™ (30%-50%, by total weight of solids) is added to the slurry. The slurry mixed for several minutes until the pigment is completely absorbed in the slurry. After absorption the RPM is raised to about 700 and cooling begins immediately to bring the temperature to 25°C - 35°C. The slurry is left to mix for about 30 minutes and then the attritor is stopped and toner including the optically variable pigment is removed.

Example 2

[0038] In an illustrative embodiment, a toner including an optically variable pigment may be prepared by preparing a mixture of a carrier liquid such as Isopar-L™ (60%-85%, by total weight), a resin such as Bynell 2020 (15%-40%, by total weight). The ingredients are mixed in a double planetary mixer, for example a Ross mixer, for about 1.5 hours at a temperature between 120° C to 160° C to produce a slurry of the carrier and polymer particles plasticized by solvation of the liquid carrier. The mixing is then continued for another 1.5 hours while the mixture cools down to room temperature. The slurry (50%-90%, by total weight of solids) is then added to a 750 ml attritor (e.g., a Union Process™ MODEL 01-HD ATTRITOR) together with a charge adjuvant like aluminum tristearate (1%-5%, by total weight of solids). Isopar-L™ can be added to adjust the viscosity of the slurry. The slurry is ground for 5 hours at 50°C-60°C at about 700 RPM. After this the RPM is lowered to about 50 RPM and a pigment such as Thermochromic BT-31™ (30%-50%, by total weight of solids) is added to the slurry. The slurry mixed for several minutes until the pigment is completely absorbed in the slurry. After absorption the RPM is raised to about 700 and cooling begins immediately to bring the temperature to 25°C - 35°C. The slurry is left to mix for about 30 minutes and then the attritor is stopped and toner including the thermochromic pigment is removed.

Example 3

[0039] In an illustrative embodiment, a toner including an optically variable pigment may be prepared by preparing a mixture of a carrier liquid such as Isopar-L™ (60%-85%, by total weight), a resin such as Nucrel™ 903 (15%-40%, by total weight). The ingredients are mixed in a double planetary mixer, for example a Ross mixer, for about 1.5 hours at a temperature between 120° C to 160° C to produce a slurry of the carrier and polymer particles plasticized by solvation of the liquid carrier. The mixing is then continued for another 1.5 hours while the mixture cools down to room temperature. The slurry (50%-90%, by total weight of solids) is then added to a 750 ml attritor (e.g., a Union Process™ MODEL 01-HD ATTRITOR) together with a charge adjuvant like aluminum tristearate (1%-5%, by total weight of solids). Isopar-L™ can be added to adjust the viscosity of the slurry. The slurry is ground for 5 hours at 50°C-60°C at about 700 RPM. After this the RPM is lowered to about 50 RPM and a pigment such as PhotoChromic VL-70S™ (30%-50%, by total weight of solids) is added to the slurry. The slurry mixed for several minutes until the pigment is completely absorbed in the slurry. After absorption the RPM is raised to about 700 and cooling begins immediately to bring the temperature to 25°C - 35°C. The slurry is left to mix for about 30 minutes and then the attritor is stopped and toner including the PhotoChromic pigment is removed.

Example 4

[0040] In an illustrative embodiment, a toner including an optically variable pigment may be prepared by preparing a mixture of a carrier liquid such as Isopar-L™ (60%-85%, by total weight), a resin such as Bynell 2020 (12%-32%, by

total weight), and Nucrel™ 699 (3%-8%, by total weight). The ingredients are mixed in a double planetary mixer, for example a Ross mixer, for about 1.5 hours at a temperature between 120° C to 160° C to produce a slurry of the carrier and polymer particles plasticized by solvation of the liquid carrier. The mixing is then continued for another 1.5 hours while the mixture cools down to room temperature. The slurry (50%-90%, by total weight of solids) is then added to a 750 ml attritor (e.g., a Union Process™ MODEL 01-HD ATTRITOR) together with a charge adjuvant like aluminum tristearate (1%-5%, by total weight of solids). Isopar-L™ can be added to adjust the viscosity of the slurry. The slurry is ground for 5 hours at 50°C-60°C at about 700 RPM. After this the RPM is lowered to about 50 RPM and a pigment such as Covapearl Sparkling Silver 937 AS™ (30%-50%, by total weight of solids) is added to the slurry. The slurry mixed for several minutes until the pigment is completely absorbed in the slurry. After absorption the RPM is raised to about 700 and cooling begins immediately to bring the temperature to 25°C - 35°C. The slurry is left to mix for about 30 minutes and then the attritor is stopped and toner including the optically variable pigment is removed.

Example 5

[0041] In an illustrative embodiment, a toner including a phosphorescent pigment may be prepared by preparing a mixture of a carrier liquid such as Isopar-L™ (60%-85%, by total weight), a resin such as Aclyn 295 (12%-32%, by total weight). The ingredients are mixed in a double planetary mixer, for example a Ross mixer, for about 1.5 hours at a temperature between 120° C to 160° C to produce a slurry of the carrier and polymer particles plasticized by solvation of the liquid carrier. The mixing is then continued for another 1.5 hours while the mixture cools down to room temperature. The slurry (50%-90%, by total weight of solids) is then added to a 750 ml attritor (e.g., a Union Process™ MODEL 01-HD ATTRITOR) together with a charge adjuvant like aluminum tristearate (1%-5%, by total weight of solids). Isopar-L™ can be added to adjust the viscosity of the slurry. The slurry is ground for 5 hours at 50°C-60°C at about 700 RPM. After this the RPM is lowered to about 50 RPM and a pigment such as Phosphor H10™ (30%-50%, by total weight of solids) is added to the slurry. The slurry mixed for several minutes until the pigment is completely absorbed in the slurry. After absorption the RPM is raised to about 700 and cooling begins immediately to bring the temperature to 25°C - 35°C. The slurry is left to mix for about 30 minutes and then the attritor is stopped and toner including the phosphorescent pigment is removed. This produces a double-security ink that glows in the dark (phosphorescent effect) and is luminescent as a green color in the visible range under UV light.

Example 6

[0042] In an illustrative embodiment, a toner including a phosphorescent pigment may be prepared by preparing a mixture of a carrier liquid such as Isopar-L™ (60%-85%, by total weight), a resin such as Nucrel 699 (12%-32%, by total weight). The ingredients are mixed in a double planetary mixer, for example a Ross mixer, for about 1.5 hours at a temperature between 120° C to 160° C to produce a slurry of the carrier and polymer particles plasticized by solvation of the liquid carrier. The mixing is then continued for another 1.5 hours while the mixture cools down to room temperature. The slurry (50%-90%, by total weight of solids) is then added to a 750 ml attritor (e.g., a Union Process™ MODEL 01-HD ATTRITOR) together with a charge adjuvant like aluminum tristearate (1%-5%, by total weight of solids). Isopar-L™ can be added to adjust the viscosity of the slurry. The slurry is ground for 5 hours at 50°C-60°C at about 700 RPM. After this the RPM is lowered to about 50 RPM and a pigment such as Phosphorescent pigment Luminova GLL-300 FFS™ (30%-50%, by total weight of solids) is added to the slurry. The slurry mixed for several minutes until the pigment is completely absorbed in the slurry. After absorption the RPM is raised to about 700 and cooling begins immediately to bring the temperature to 25°C - 35°C. The slurry is left to mix for about 30 minutes and then the attritor is stopped and toner including the phosphorescent pigment is removed. This produces a double security ink that glows in the dark (phosphorescent effect) and is luminescent in a green color in the visible range under UV light.

Example 7

[0043] In an illustrative embodiment, a toner including a phosphorescent pigment may be prepared by preparing a mixture of a carrier liquid such as Isopar-L™ (60%-85%, by total weight), a resin such as Lotader 8200 (12%-32%, by total weight). The ingredients are mixed in a double planetary mixer, for example a Ross mixer, for about 1.5 hours at a temperature between 120° C to 160° C to produce a slurry of the carrier and polymer particles plasticized by solvation of the liquid carrier. The mixing is then continued for another 1.5 hours while the mixture cools down to room temperature. The slurry (50%-90%, by total weight of solids) is then added to a 750 ml attritor (e.g., a Union Process™ MODEL 01-HD ATTRITOR) together with a charge adjuvant like aluminum tristearate (1%-5%, by total weight of solids). Isopar-L™ can be added to adjust the viscosity of the slurry. The slurry is ground for 5 hours at 50°C-60°C at about 700 RPM. After this the RPM is lowered to about 50 RPM and a pigment such as Glacierglo GG25X1009 Blue/Green™ (30%-50%, by total weight of solids) is added to the slurry. The slurry mixed for several minutes until the pigment is completely absorbed

in the slurry. After absorption the RPM is raised to about 700 and cooling begins immediately to bring the temperature to 25°C - 35°C. The slurry is left to mix for about 30 minutes and then the attritor is stopped and toner including the phosphorescent pigment is removed. This produces an electroluminescent ink.

[0044] It should be noted that ratios, concentrations, amounts, and other numerical data may be expressed herein in a range format. It is to be understood that such a range format is used for convenience and brevity, and thus, should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. To illustrate, a concentration range of "about 0.1 % to about 5%" should be interpreted to include not only the explicitly recited concentration of about 0.1 wt% to about 5 wt%, but also include individual concentrations (e.g., 1%, 2%, 3%, and 4%) and the sub-ranges (e.g., 0.5%, 1.1%, 2.2%, 3.3%, and 4.4%) within the indicated range.

[0045] Many variations and modifications may be made to the above-described embodiments. All such modifications and variations are intended to be included herein within the scope of this disclosure and protected by the following claims.

Claims

1. A method of forming an ink toner comprising:

mixing a carrier liquid and a resin to form a slurry;
grinding the slurry for 1 to 5 hours at 50° C to 60° C at 500 to 800 revolutions per minute (RPM);
reducing the grinding to 25 to 150 RPM;
adding a pigment to the slurry and grind until the pigment is absorbed in the slurry to form a slurry/pigment mixture, wherein the pigment is selected from optically variable pigments, thermochromic pigments, photochromic pigments, photoluminescent pigments, phosphorescent pigments, electroluminescent pigments, and combinations thereof; and
grinding the slurry/pigment mixture at 500 to 800 RPM for 15 to 45 minutes at 25° C to 35° C to form the ink toner.

2. The method of claim 1, wherein the carrier liquid carrier is selected from a compound having the following characteristics: a resistivity in excess of 10^9 ohm-cm and a dielectric constant below 3.0.

3. The method of claim 1, wherein the resin comprises a thermoplastic toner resin.

4. The method of claim 1, wherein the pigment is selected from the group consisting of an optically variable pigment; a thermochromic pigment; a photochromic pigment; and a photoluminescent pigment.

5. The method of claim 1, wherein reducing the grinding comprises: reducing the grinding to 25 to 100 RPM.

6. The method of claim 1, wherein reducing the grinding comprises: reducing the grinding to 40 to 60 RPM.

7. The method of claim 1, wherein grinding the slurry/pigment mixture comprises:

grinding the slurry/pigment mixture at 500 to 750 RPM for 25 to 35 minutes at 25° C to 35° C to form the ink toner.

8. The method of claim 1, wherein grinding the slurry further comprises:

adding a charge adjuvant to the slurry.

9. The method of claim 1, wherein the grinding is performed in an attritor.

10. The method of claim 1, wherein mixing a carrier liquid and a resin to form a slurry further comprises:

mixing the carrier liquid and the resin for 1 to 2 hours at 120° C to 160° C; and
mixing the carrier liquid and the resin for 1 to 2 hours to cool the mixture to 25° C to 35° C.

11. The method of claim 1, further comprising making an ink composition comprising the ink toner resulting from the method of claim 1.

12. The method of claim 11, where the pigment is selected from: metal effect pigments, interference pigments, luster pigments, goniochromatic pigments, pearlescent pigments, and combinations thereof.

Patentansprüche

1. Verfahren zum Bilden eines Tintentoners, umfassend
Vermischen einer Trägerflüssigkeit und eines Harzes zur Bildung einer Verschlammung;
Mahlen der Verschlammung für 1 bis 5 Stunden bei 50°C bis 60°C bei 500 bis 800 Umdrehungen pro Minute (U/min);
Verringern des Mahlens auf 25 bis 150 U/min;
Zusetzen eines Pigments zur Verschlammung und Mahlen bis das Pigment in die Verschlammung absorbiert ist, zur Bildung einer Verschlammung-Pigment-Mischung, wobei das Pigment ausgewählt ist aus optisch variablen Pigmenten, thermochromischen Pigmenten, photochromen Pigmenten, photolumineszenten Pigmenten, phosphoreszierenden Pigmenten, elektrolumineszenten Pigmenten und Kombinationen davon; und
Mahlen der Verschlammung-Pigment-Mischung bei 500 bis 800 U/min für 15 bis 45 Minuten bei 25°C bis 35°C zum Bilden des Tintentoners.
2. Verfahren gemäß Anspruch 1, wobei die Trägerflüssigkeit ausgewählt ist aus einer Verbindung mit den folgenden Eigenschaften: eine Resistivität von über 10^9 Ohm-cm und eine Dielektrizitätszahl unter 3,0.
3. Verfahren gemäß Anspruch 1, wobei das Harz ein thermoplastisches Tonerharz umfasst.
4. Verfahren gemäß Anspruch 1, wobei das Pigment ausgewählt ist aus der Gruppe bestehend aus einem optisch variablen Pigment, einem thermochromischen Pigment, einem photochromen Pigment und einem photolumineszenten Pigment.
5. Verfahren gemäß Anspruch 1, wobei Verringern des Mahlens umfasst Verringern des Mahlens auf 25 bis 100 U/min.
6. Verfahren gemäß Anspruch 1, wobei Verringern des Mahlens umfasst Verringern des Mahlens auf 40 bis 60 U/min.
7. Verfahren gemäß Anspruch 1, wobei Mahlen der Verschlammung-Pigment-Mischung umfasst
Mahlen der Verschlammung-Pigment-Mischung bei 500 bis 750 U/min für 25 bis 35 Minuten bei 25°C bis 35°C zum Bilden des Tintentoners.
8. Verfahren gemäß Anspruch 1, wobei Mahlen der Verschlammung zudem umfasst
Zusetzen eines Ladungshilfsstoffs zur Verschlammung.
9. Verfahren gemäß Anspruch 1, wobei das Mahlen in einer Reibungsmühle erfolgt.
10. Verfahren gemäß Anspruch 1, wobei das Vermischen einer Trägerflüssigkeit und eines Harzes zum Bilden einer Verschlammung zudem umfasst
Vermischen der Trägerflüssigkeit und des Harzes für 1 bis 2 Stunden bei 120°C bis 160°C, und
Vermischen der Trägerflüssigkeit und des Harzes für 1 bis 2 Stunden zum Kühlen der Mischung auf 25°C bis 35°C.
11. Verfahren gemäß Anspruch 1, zudem umfassend Herstellen einer Tintenzusammensetzung, umfassend den Tintoner, erhalten aus dem Verfahren aus Anspruch 1.
12. Verfahren gemäß Anspruch 11, wobei das Pigment ausgewählt ist aus: Metalleffektpigmente, Interferenzpigmente, Glanzpigmente, goniochromatische Pigmente, Perlglanzpigmente und Kombinationen davon.

Revendications

1. Procédé de formation d'un toner d'encre comprenant :
le mélange d'un liquide porteur et d'une résine pour former une pâte ;
le broyage de la pâte pendant 1 à 5 heures à 50°C à 60°C à 500 à 800 tours par minute (RPM) ;
la réduction du broyage à 25 à 150 RPM ;

l'addition d'un pigment à la pâte et le broyage jusqu'à ce que le pigment soit absorbé dans la pâte pour former un mélange pâte/pigment, dans lequel le pigment est sélectionné parmi des pigments optiquement variables, des pigments thermochromiques, des pigments photochromiques, des pigments photoluminescents, des pigments phosphorescents, des pigments électroluminescents et des combinaisons de ceux-ci ; et le broyage du mélange pâte/pigment à 500 à 800 RPM pendant 15 à 45 minutes à 25°C à 35°C pour former le toner d'encre.

2. Procédé selon la revendication 1, dans lequel le liquide porteur est sélectionné parmi un composé ayant les caractéristiques suivantes : une résistivité dépassant 10^9 ohm-cm et une constante diélectrique inférieure à 3,0.

3. Procédé selon la revendication 1, dans lequel la résine comprend une résine de toner thermoplastique.

4. Procédé selon la revendication 1, dans lequel le pigment est sélectionné parmi le groupe constitué d'un pigment optiquement variable ; d'un pigment thermochromique ; d'un pigment photochromique ; et d'un pigment photoluminescent.

5. Procédé selon la revendication 1, dans lequel la réduction du broyage comprend : la réduction du broyage à 25 à 100 RPM.

6. Procédé selon la revendication 1, dans lequel la réduction du broyage comprend : la réduction du broyage à 40 à 60 RPM.

7. Procédé selon la revendication 1, dans lequel le broyage du mélange pâte/pigment comprend :

le broyage du mélange pâte/pigment à 500 à 750 RPM pendant 25 à 35 minutes à 25°C à 35°C pour former le toner d'encre.

8. Procédé selon la revendication 1, dans lequel le broyage de la pâte comprend en outre :

l'addition d'un adjuvant de charge à la pâte.

9. Procédé selon la revendication 1, dans lequel le broyage est réalisé dans un broyeur à attrition.

10. Procédé selon la revendication 1, dans lequel le mélange d'un liquide porteur et d'une résine pour former une pâte comprend en outre :

le mélange du liquide porteur et de la résine pendant 1 à 2 heures à 120°C à 160°C ; et

le mélange du liquide porteur et de la résine pendant 1 à 2 heures pour refroidir le mélange à 25°C à 35°C.

11. Procédé selon la revendication 1, comprenant en outre la fabrication d'une composition d'encre comprenant le toner d'encre résultant du procédé selon la revendication 1.

12. Procédé selon la revendication 11, où le pigment est sélectionné parmi : des pigments à effet métallique, des pigments d'interférence, des pigments brillants, des pigments goniochromatiques, des pigments perlés et des combinaisons de ceux-ci.

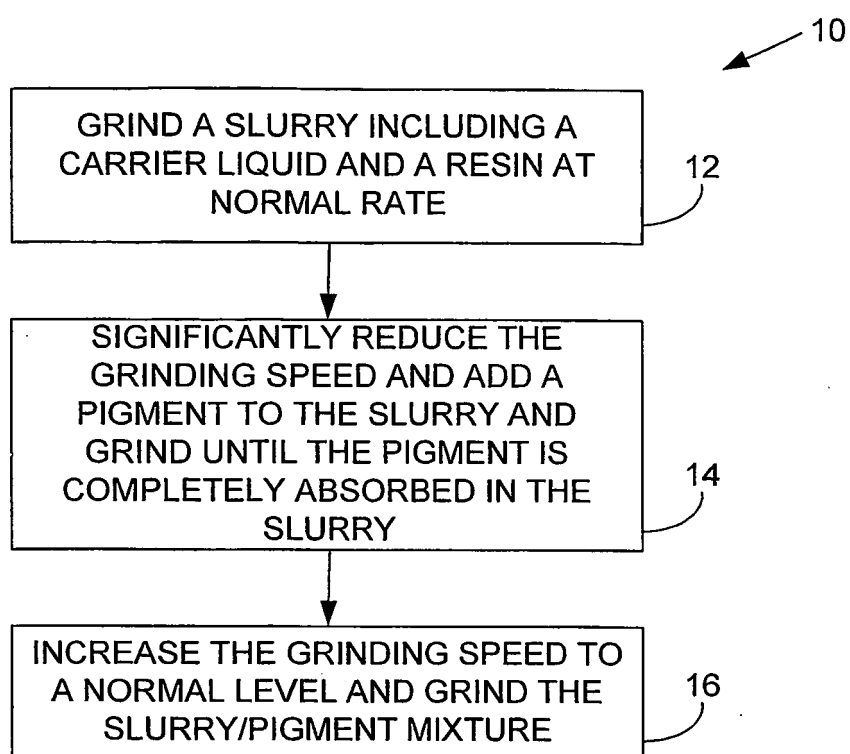


FIG. 1

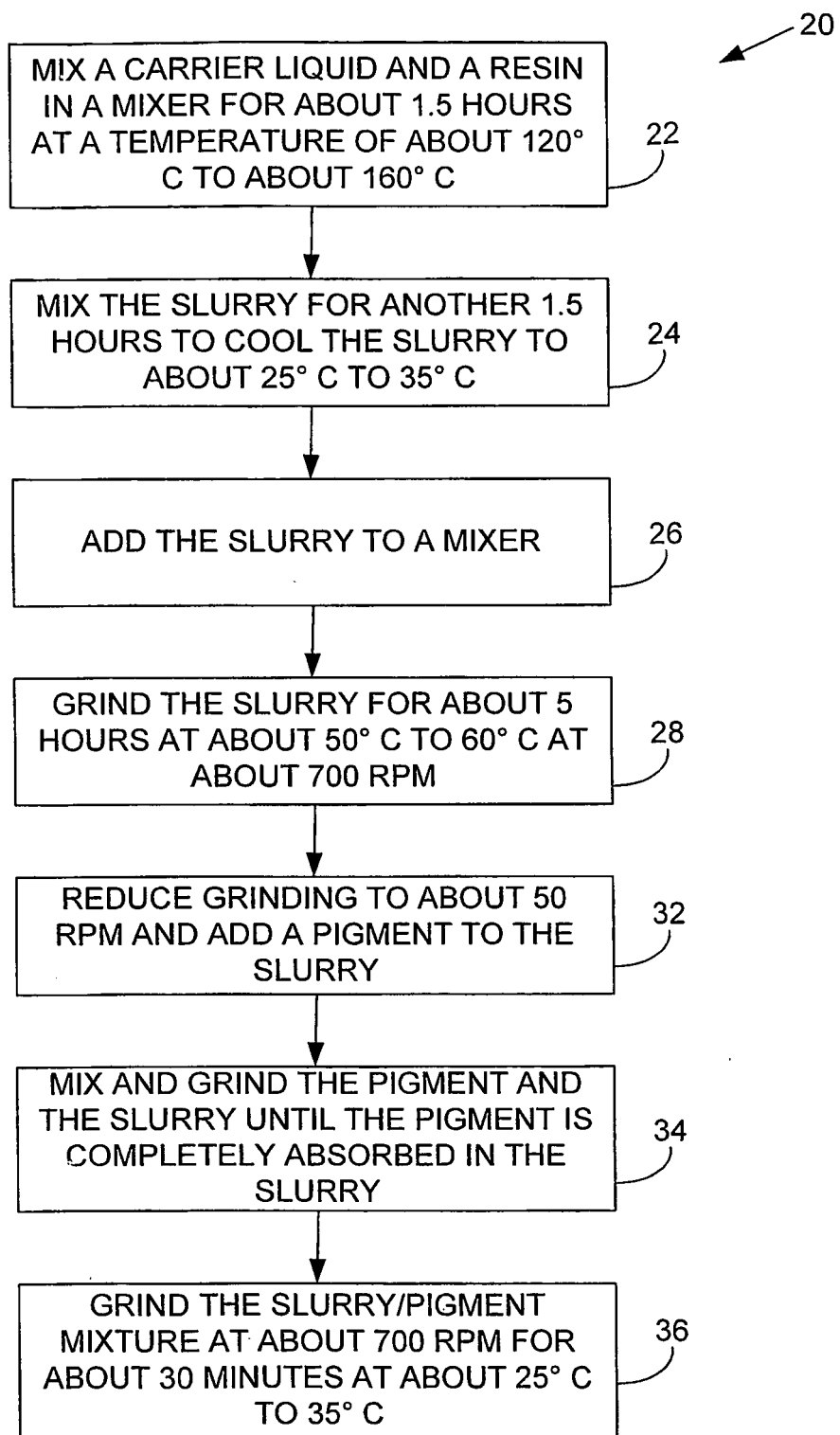


FIG. 2

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 4794651 A [0002]
- US 4842974 A [0002]
- US 5047306 A [0002]
- US 5407307 A [0002]
- US 5192638 A [0002]
- US 5208130 A [0002] [0003]
- US 5225306 A [0002]
- US 5264312 A [0002]
- US 5266435 A [0002] [0003]
- US 5286593 A [0002]
- US 5300390 A [0002]
- US 5346796 A [0002]
- US 5407771 A [0002]
- US 5554476 A [0002]
- US 5655194 A [0002]
- US 5792584 A [0002]
- US 55923929 B [0002]
- WO 9217823 A [0002]
- US 4678317 A [0003]
- US 4860924 A [0003]
- US 4980259 A [0003]
- US 4985732 A [0003]
- US 5028964 A [0003]
- US 5034778 A [0003]
- US 5047808 A [0003]
- US 5078504 A [0003]
- US 5117263 A [0003]
- US 5148222 A [0003]
- US 5157238 A [0003]
- US 5166734 A [0003]
- US 5231454 A [0003]
- US 5255058 A [0003]
- US 5268687 A [0003]
- US 5270776 A [0003]
- US 5276492 A [0003]
- US 5278615 A [0003]
- US 5280326 A [0003]
- US 5286948 A [0003]
- US 5289238 A [0003]
- US 5315321 A [0003]
- US 5335054 A [0003]
- US 5337131 A [0003]
- US 5376491 A [0003]
- US 5380611 A [0003]
- US 5426491 A [0003]
- US 5436706 A [0003]
- US 5497222 A [0003]
- US 5508790 A [0003]
- US 5527652 A [0003]
- US 5552875 A [0003]
- US 5555185 A [0003]
- US 5557376 A [0003]
- US 5558970 A [0003]
- US 5570193 A [0003]
- US 6117606 A [0004]
- DE 1467468 [0029]
- DE 1959998 [0029]
- DE 2009566 [0029]
- DE 2214545 [0029]
- DE 2215191 [0029]
- DE 2244298 [0029]
- DE 2313331 [0029]
- DE 2522572 [0029]
- DE 3137808 [0029]
- DE 3137809 [0029]
- DE 3151343 [0029]
- DE 3151354 [0029]
- DE 3151355 [0029]
- DE 3211602 [0029]
- DE 3253017 [0029]